[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE TEMPERATURE COEFFICIENT OF THE SYNTHESIS OF HYDROGEN CHLORIDE BY LIGHT AND BY ALPHA-RADIATION

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In 1926, Porter, Bardwell, and Lind[1] compared the rates of hydrogen chloride synthesis by light and by α-rays at 25°. The method consisted in circulating the same mixture of hydrogen and chlorine through a light chamber and through an α-ray chamber, employing in the latter radon in a thin α-ray bulb. The principal result was the discovery that any change in sensitivity of the gas mixture toward one form of activation was exactly the same as for the other. This result is readily interpreted in terms of chain mechanism, as meaning that by no matter what agency a chain is initiated, its further propagation depends only on the gas mixture and its sensitivity (concentration of inhibitors which terminate the chains). This primary result is confirmed in the present work.

The absolute value of the ratio of the yield per ion pair to that per light quantum, which Porter, Bardwell and Lind[1] found equal to nearly 4, has not been wholly confirmed, but a value approximating unity has been obtained. This discrepancy may be partly due to the fact that in the present photochemical experiments a strictly monochromatic source was used for the quantum yield measurements, whereas in the work of Porter, Bardwell and Lind a considerable fraction of the chlorine absorption band was involved. As Allmand and Beesley[2] have recently shown, the different wave lengths absorbed are by no means equal in efficiency in causing synthesis of hydrogen chloride. When correction is made by using Allmand and Beesley's data[2a], the values are reduced from unity and 3.7 to slightly less than unity and to approximately 2.5, respectively. We have at present no explanation for this three-fold discrepancy.

In the paper of Porter, Bardwell and Lind[1] it was found that the photochemical yield per quantum increased about two-fold in the interval 25–100°. On the assumption that the α-ray reaction, in analogy to most of the other reactions previously studied, would be independent of temperature, it was concluded that the M/N and $M/h\nu$ yields might approach each other at high temperatures. Experiment has shown the danger of faulty analogy, since sight was lost of the fact that none of the supposedly analogous α-ray reactions had chain mechanisms, and that if the temperature coefficient is largely determined by the chain part of the reaction, as predicted by Cremer,[3] then the α-ray and light reactions should possess

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[1] Porter, Bardwell and Lind, THIS JOURNAL, **48,** 2603 (1926).

[2] (a) Allmand and Beesley, *Nature,* **123,** 164 (1929); see also (b) Coehn and Jung, *Z. physik. Chem.,* **110,** 705 (1924).

[3] E. Cremer, *ibid.,* **128,** 285 (1927).

identical temperature coefficients. The present experiments show this to be the case for white light.

This conclusion must be contrasted with Tolman's[4] theory of the temperature coefficient as a function of the primary rather than the secondary step in the reaction. If each wave length has its own temperature coefficient, the greater the smaller the quantum, then only by accident will any one of these or the average of all coincide with the α-ray temperature coefficient. More drastic comparison with "green light" ($NiSO_4$ filter) over the same temperature range showed a temperature coefficient of 1.3 for a 10° interval, which is distinctly higher than 1.2, the value for white light in the same region of sensitivity. This may mean that Tolman's theory[4] is not incorrect in principle, but that actually the temperature coefficient is determined almost entirely by one or more steps in the chain mechanism rather than in the primary step.

Porter, Bardwell and Lind[1] also found that the temperature coefficient is a function of the sensitivity, becoming greater the higher the sensitivity. This has been confirmed, but their case of an actual negative coefficient at very low sensitivity could not be substantiated. The actual value of the 10° coefficient is higher by about 0.1 than that of Porter, Bardwell and Lind; the maximum is lower than that of Padoa and Butironi[5] for white light, but is in good agreement with the average of Bevan's values.[6]

Apparatus and Calibration

The apparatus used was a modified Bunsen and Roscoe actinometer,[7] similar to that employed by Porter, Bardwell and Lind.[1] The essential parts of the apparatus, a diagram of which is given in Fig. 1, are an electrolytic generator, a capillary U-tube trap containing a few drops of water, a magnetic circulating pump, an absorption vessel, two reaction chambers in separate thermostats and a graduated capillary actinometer. The entire apparatus was made of pyrex glass.

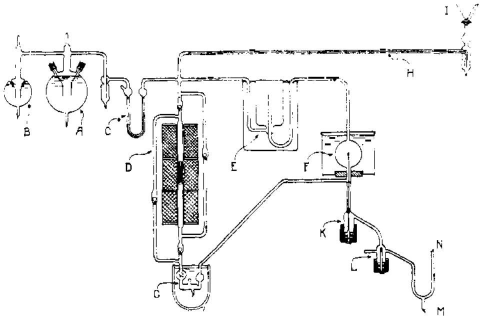

Fig. 1.—Diagram of the apparatus.

The generator A contains concentrated hydrochloric acid. The electrodes are of platinum–iridium alloy and are introduced through small rubber stoppers, which are covered outside by mercury seals. The generator B contains dilute sulfuric acid and was used to generate a hydrogen–oxygen mixture, when it was desired to decrease the sensitivity of the gaseous mixture. Since the amount of oxygen added was always a

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[4] Tolman, This Journal, **42,** 2506 (1920); **45,** 2285 (1923).

[5] Padoa and Butironi, *Gazz. chim. ital.*, **47,** II, 6 (1917).

[6] Bevan, *Proc. Camb. Phil. Soc.*, **12,** 398 (1904).

[7] Bunsen and Roscoe, *Pogg. Ann.*, **100,** 43 (1857).

small fraction of the total amount of gas, the effect of the hydrogen added simultaneously was negligible.

The trap C was used to isolate the generator while measurements were being made. The capillary U-tube is constricted at one point so that a drop of solution can be held there by surface tension.[8] By immersing the trap in liquid air a plug of solid chlorine and ice is formed, which permits the reaction system to be pumped out, through J, without affecting the generator.

The photochemical reaction cell E is similar in design and size to that used by Porter, Bardwell and Lind.[1] The radiochemical reaction cell is a sphere 5.0 cm. in (inside) diameter, having an α-ray bulb mounted at its center. In order that it might be sealed to the apparatus the α-ray bulb was made of pyrex. This can be done quite readily by a technique differing only slightly from that described by Lind.[9] The bulbs were blown in a quartz furnace heated with a gas–oxygen flame, using compressed air (at approximately 6-lb. pressure) instead of a foot bellows.

Radon was introduced into the apparatus sealed in a thin capillary, which was placed through the "eye" in the top of the central steel rod in the breaking vessel L. The capillary was broken by revolving the rod, which extended through a hard rubber stuffing gland and a double mercury seal. After breaking the capillary the radon was condensed just below the reaction bulb by means of liquid air in a Ramsay liquid air funnel. The mercury was then brought just below the radon, before it was released by warming, to minimize absorption or trapping along the wall. The setting valve F is a modification of that described by Lind.[9]

The circulating pump was of the type described by Livingston,[10] and was capable of producing a rapid regular rate of flow.

The capillary used for the actinometer was selected for uniformity by measuring the length of a thread of mercury at different points along its length. It was calibrated by determining the length of a thread of mercury of known weight.

The quantity of radon used was determined by the gamma-ray method by comparison with a standard tube certified by the Bureau of Standards.

A 75-watt gas-filled tungsten lamp, situated one meter from the reaction cell was used as a secondary standard in the determination of the temperature coefficient of the radiochemical reaction. In the determination of the temperature coefficient of the photochemical reaction 75- and 200-watt lamps were used. They were run on 109 volts a. c., the voltage across the lamp being maintained by a hand regulated series resistance. In some of the experiments blackened copper gauzes were used to reduce the intensity of the light.

The monochromatic source, used as a radiation standard, consisted of a quartz mercury arc, equipped with the lenses and diaphragms necessary to produce a gradually converging pencil of light. The light beam passed through Corning filters G585 and G38 and a crown glass absorption cell containing a 5% copper chloride solution. The emitted radiation was practically pure monochromatic light of 4358 Å. The arc was run at 52 volts and 3.0 amperes d. c. Variations in the line voltage and the room temperature were counterbalanced by an adjustable series resistance and forced ventilation of the lamp housing. The constancy of energy emitted was checked by direct measurement on several occasions during the course of the work.

The energy measurements were made with a Moll thermopile and a sensitive low-

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[8] Compare Ref. 1, p. 2607.

[9] Lind, "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., New York, **1928**, pp. 86–88.

[10] Livingston, *J. Phys. Chem.*, **33**, 955 (1929). The drawing in this article is printed upside down.

resistance Leeds and Northrup galvanometer. Deflections were observed on a ground glass scale placed one meter from the galvanometer. The system was calibrated by means of a radiation standard lamp furnished by the Bureau of Standards, for which the total radiation in absolute units at two meters distance in a given direction was known for various values of the current. When the calibrations were made a 15-ohm resistance was put in series with the galvanometer to reduce the deflection. Following the explicit directions furnished with the lamp, the results summarized in the following table were obtained.

TABLE I

CALIBRATION OF THE THERMOPILE AND GALVANOMETER

Amperes through filament[a]	Ergs mm.² sec.[b]	Average deflection	Ergs/per mm. deflection mm.² sec.
0.250	4.26	20.20	0.02109
.300	6.27	29.87	.02099
.350	8.67	41.00	.02115
		Av.	.02108 ± 0.00007

[a] The ammeter used in these measurements was kindly calibrated by Professor A. Zeleny of the Department of Physics. [b] Calibration of the Bureau of Standards for flux at 2 meters' distance from the lamp.

The deflections given in Column 4 are the averages of a large number of observations. The inside diameter of the thermopile horn is 2.60 cm. Assuming that all of the light falling in the horn is reflected onto the elements[11] the sensitivity of the system may be computed directly, as $0.02108 \times (26.0/2) \times \pi = 11.19$ ergs/sec. per mm. deflection. Since the thermopile was equipped with a fluorite window, it is necessary to apply a correction for its absorption of the total radiation incident. If we take an approximate value for the transmission as 91%, the corrected value for the sensitivity is 10.18. Since the measurements of the energy of the monochromatic source were made with no extra resistance in the circuit, a correction must be applied for the 15 ohms used in calibration. A series of direct comparisons showed this factor to be equal to 0.677. The final value for the calibration is 6.89 ergs/sec. per mm. deflection.

The Temperature Coefficient of the Photochemical Reaction.—The apparatus used in the determination of the temperature coefficient of the photochemical reaction differed from that represented in Fig. 1 in that a second photochemical vessel (similar to the first) was introduced in place of the radiochemical vessel. These vessels were surrounded by separate thermostats, one of which was kept at room temperature, while the other was maintained at either room temperature or at 94°.

Reaction velocity measurements were made by illuminating alternately the first and second reaction vessels. In order to avoid the lag which follows a change in the intensity of activation, the method which Porter, Bardwell and Lind used for slow reactions[12] was not employed. The following method was adopted. Reaction Vessel I was illuminated, and the time required for the meniscus to move through a certain 50 cm. length

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[11] This was demonstrated for this instrument by B. Lewis, *J. Phys. Chem.*, **32**, 278 (1928).

[12] Ref. 1, p. 2611.

of the actinometer capillary was determined; the illumination on Vessel I was shut off and Vessel II was illuminated; the meniscus was displaced by admitting more gas from the generator, and the time required for the meniscus to move through the 50 cm. length was taken. At least five such successive measurements were performed, and the average value of the ratio of the recorded times, with Vessel I and with Vessel II illuminated, was computed. The following typical computation will illustrate the method of taking the average.

TABLE II

COMPUTATION OF THE AVERAGE

A	B	C	D	E	
	201.5				
197.5		147		1.34	A/C
	193.5		140	1.38	A/D
189		133.5		1.42	A/C
	184.5		133	1.39	B/D
184		132		1.39	A/C
	183		131.5	1.39	B/D
		131			
			Av.	1.39	

Columns B and C give the times in seconds observed when Vessels I and II, respectively, were illuminated. Column A gives the averages between successive values in B, and Col. D gives the averages for C. As is indicated by the arrangement, values of B and C were determined alternately. Values of the ratio of the time required when Vessel I was illuminated are given in Column E. This term is equal to the ratio of the two reaction velocities, or, since the illumination was constant, to $(M/q)_{\mathrm{I}}/(M/q)_{\mathrm{II}}$, where M/q is the number of molecules reacting per quantum absorbed.

Rapid changes in sensitivity were never observed during the course of an experiment. A slow uniform drift in sensitivity was commonly observed (compare Table I), but did not appreciably affect the accuracy of the values of the ratio. We were unable to determine what factors were responsible for the sudden changes in sensitivity observed by Porter, Bardwell and Lind.[13] By the use of the two electrolytic generators the sensitivity could be controlled over a wide range. To increase the sensitivity the reaction system was first pumped out and then refilled by starting the hydrogen–chlorine generator (A). To reduce the sensitivity, the hydrogen–oxygen generator (B) was run for a few seconds.

To evaluate the temperature coefficient values of $(M/q)_{\mathrm{I}}/(M/q)_{\mathrm{II}}$ must be determined, first when both reactions occur at the same temperature, and second when one of them (I) occurs at a different temperature (94°). Since $(M/q)_{\mathrm{II},\,25°}$ differs from $(M/q)_{\mathrm{I},\,25°}$ only in the number of chains started per second (*i. e.*, by a constant factor), we may write

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[13] Ref. 1, p. 2611.

$$\frac{(M/q)_{94°}}{(M/q)_{25°}} = \frac{(M/q)_{\mathrm{I},\,94°}}{(M/q)_{\mathrm{II},\,25°}} \times \frac{(M/q)_{\mathrm{II},\,25°}}{(M/q)_{\mathrm{I},\,25°}}$$

The average variation of the reaction velocity per 10° interval over the range 25 to 98°, K_{10}, is given by the equation

$$\log K_{10} = \frac{10°}{94 - 25°} \log \frac{(M/q)_{94°}}{(M/q)_{25°}}$$

In computing values of K_{10} the measured room temperature, which varied from 21 to 27°, was used instead of 25°. A few measurements, Numbers 20 to 22, Table III, were made at 52°. The differences between the temperatures of the two thermostats (ΔT) is given in Col. 5. The values of $(M/q)_{94°}/(M/q)_{25°}$ listed are each based upon a series of measurements similar to that quoted in Table II. Only those series which showed a uniform drift in sensitivity, not greater than 6% between successive measurements, are recorded. The values of $(M/q)_{\mathrm{I},\,25°}/(M/q)_{\mathrm{II},\,25°}$ used in computing $(M/q)_{94°}/(M/q)_{25°}$ are each the average of from six to ten series of measurements.

In order to obtain an absolute value for the chain length, M/q, at which the temperature coefficient measurements were performed, a cylindrical absorption cell was sealed into the apparatus in place of one of the reaction vessels. The cell is 16.0 cm. long and has plane sealed-on ends 3.0-mm. thick. The monochromatic source was adjusted to throw a narrow pencil of light which passed through the cell and converged into the horn of the thermopile. Measurements were made of the energy passing through the cell when it was evacuated to less than a mm. pressure and when the reaction mixture circulated through it at one atmosphere pressure. The galvanometer deflection corresponding to the absorption by the gas was 3.20 cm. This corresponds to a rate of absorption of 6.89 ergs./sec. mm. × 32.0 mm. = 220.5 ergs./sec. This value must be corrected for the absorption by the second pyrex plate of the cell. Direct measurements with this plate, and measurements with 11.7 mm. of pyrex, gave a value for the transmission of the plate of 91%.[14] The absorption of the fluorite window for light of this wave length is practically negligible. Correcting for the absorption by the pyrex, the amount of energy absorbed is 243 ergs./sec. The energy per quantum is

$$E = \frac{6.56 \times 10^{-27} \times 3 \times 10^{10}}{4.36 \times 10^{-8}} = 4.51 \times 10^{12} \text{ ergs. per quantum}$$

Therefore, the rate of absorption of quanta is $2.43 \times 10^2/4.51 \times 10^{-12} = 5.40 \times 10^{13}$ quanta per second.

By comparing the reaction velocity due to the monochromatic source with the velocities due to the white light sources used, the number of

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[14] This corresponds to a considerably lower value for the coefficient of absorption than that based on measurements of the transmission of a plate 0.77 mm., made by Gibson and McNichols in 1919, Bureau of Standards., Technical Paper 119 (1919).

quanta absorbed by the chlorine from the latter may be computed. *Since quanta of different frequencies are not equally effective in starting reaction chains,*[2] *the number of the quanta determined in this way is not equal to the actual number of quanta absorbed from the white light, but rather to the number of quanta of λ4358 Å. which would be required to maintain the same rate.* The values of M, used in computing M/q, were obtained from the calibration of the actinometer capillary; 1.00 cm. displacement corresponds to 0.0504 cc. By combining this factor with Avogadro's number and the observed rate of displacement of the meniscus (in cm. per sec.), M, the number of molecules reacting per second can be obtained. The detailed results of the comparison of the monochromatic source with the 75-watt lamp are given in Table III.

TABLE III

COMPARISON OF A 75-WATT LAMP WITH THE MONOCHROMATIC SOURCE

$(M/q)_w/(M/q)_{4358}$	0.174	0.185	0.159	0.152	0.173	0.172	
$q \times 10^{-13}$, 4358 Å.	5.40	5.40	5.40	5.40	5.40	5.40	
$q \times 10^{-13}$, white	0.94	1.00	0.86	0.82	0.94	0.93	Av. 0.92 ± 0.05
$M/q \times 10^{-13}$	16	18	23	39	43	49	

The other white light sources were compared to the 75-watt lamp in a similar manner. The number of quanta absorbed per second for each of these is indicated in Col. 3 of Table IV.

TABLE IV

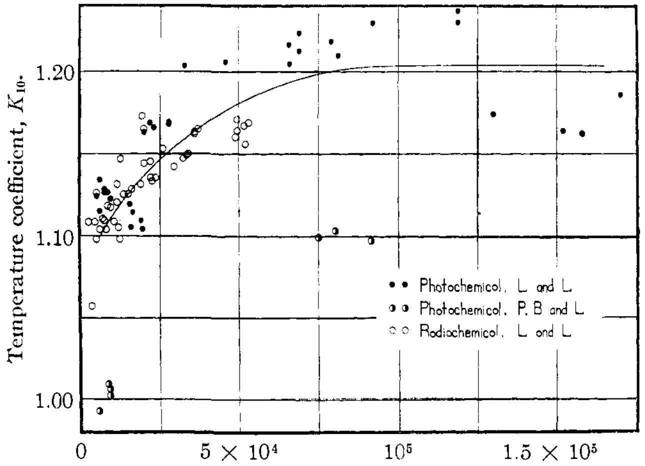
TEMPERATURE COEFFICIENT OF THE PHOTOCHEMICAL REACTION

		$(M/q)_{94°}/(M/q)_{25°}$				
Number	$q \times 10^{-13}$	Obs.	Corr.	$\Delta T°$	$M/q \times 10^{-3}$	K_{10}
1	2.45	2.09	2.26	69	5.1	1.124
2	2.45	2.25	2.43	70	5.8	1.134
3	2.45	1.99	2.05	70	6.1	1.115
4	2.45	2.03	2.19	65	7.4	1.126
5	2.45	2.14	2.31	68	7.4	1.128
6	2.45	2.12	2.29	69	8.6	1.126
7	2.45	2.00	2.16	71	9.4	1.122
8	2.45	2.03	2.19	69	15.5	1.119
9	2.45	1.84	1.99	68	16	1.105
10	2.45	1.95	2.11	68	16.5	1.114
11	2.45	1.88	2.03	67	19	1.109
12	2.45	1.82	1.97	67	19.5	1.104
13	0.92	2.58	2.79	67	20	1.163
14	.92	2.67	2.88	67	22	1.169
15	.92	2.66	2.87	68	23	1.166
16	.92	2.69	2.91	68	28	1.168
17	.92	2.71	2.93	68	28	1.169
18	.256	3.12	3.37	67	33	1.204
19	.256	3.26	3.62	69	46	1.206
20	.256	1.69	1.74	28	66	1.217
21	.256	1.64	1.69	28	66	1.205

TABLE IV (*Concluded*)

Number	$q \times 10^{-13}$	$(M/q)_{94°}/(M/q)_{25°}$		$\Delta T°$	$M/q \times 10^{-3}$	K_{10}
		Obs.	Corr.			
22	0.256	1.67	1.72	28	69	1.213
23	.256	3.76	4.06	67	69	1.224
24	.256	3.47	3.75	68	79	1.219
25	.256	3.35	3.62	69	81	1.210
26	.256	3.71	4.01	68	92	1.230
27	.167	4.33	4.68	72	119	1.238
28	.167	4.10	4.43	71	119	1.231
29	.167	2.78	3.00	68	130	1.174
30	.167	2.57	2.78	67	152	1.164
31	.167	2.55	2.75	67	158	1.162
32	.167	2.93	3.16	67	170	1.186

In Fig. 2 the values of K_{10} are plotted (as black dots) against the average chain length, M/q. As may be readily seen from this plot, the value of K_{10} depends on the sensitivity, or average chain length. It is least for low sensitivities and rises to a constant value or flat maximum for M/q equal to 10^5.



Average chain length, M/q or M/N.

Fig. 2.—The temperature coefficient.

Since it proved difficult to attain the highest sensitivities, comparatively few measurements were made for chain lengths greater than 10^5, and it is possible that the values of K_{10} corresponding to the highest sensitivities are less accurate than those in the intermediate range. It should be noted that these values are not in agreement with those published by Porter, Bardwell and Lind[1] (which are indicated by half-blackened circles in Fig. 2), although both sets of data show the same trend with sensitivity. The explanation of this discrepancy is not known.

It should be of interest to compare the values of the temperature coefficient given here with those published by other investigators.[1,5,6] Since these measurements were made for different temperature intervals, probably the simplest way of comparing them is to plot the logarithm of the reaction velocity against the absolute temperature. Such a plot is given in Fig. 3. Arbitrary quantities have been added to each of the several series of values of log v such that they coincide at $T = 298°K$. The values taken from Table IV are the average of Numbers 20, 21 and 22 for 52°, and Number 23 for 94°; these values correspond to an average chain length of about 68,000. All of the values plotted represent experiments with white light. The values taken from the work of Porter, Bardwel and Lind correspond to a chain length of about 80,000. Except for the values of Porter, Bardwell and Lind, all of the results are in as good agreement as could be expected, particularly when it is remembered that the sensitivity of the mixtures used by Bevan[6] and by Padoa and Butironi[5] are not known. The data also indicate that the Arrhenius equation holds at least approximately for this reaction. In view of the complex nature of the reaction, this latter result is rather surprising.

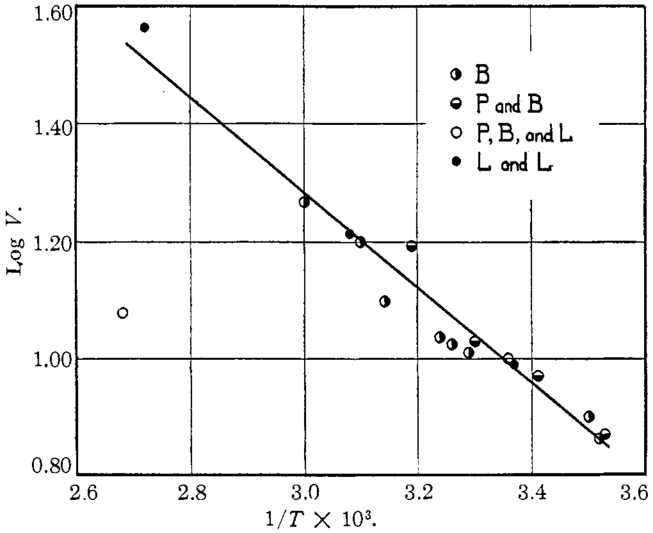


Fig. 3.—Comparison of rate measurements at different temperatures.

The results of Padoa and Butironi[5] indicate that the value of K_{10} is greatly affected by the wave length of the absorbed light. To test this result a few measurements were made with a 100-watt light and a 5-cm. filter of saturated nickel sulfate solution. The values of the temperature coefficient so obtained were unmistakably larger; about 1.29 for $M/q = 10^5$. However, this is much smaller than the value of 1.5 obtained by

Padoa and Butironi. The results of these latter experimenters may be influenced by their experimental conditions. If their reaction was preceded by an induction period of measurable length, then reducing the number of effective quanta absorbed per second, as in going to light of longer wave length by means of filters, would very probably produce an apparent increase in the temperature coefficient. In a recent preliminary report, Allmand and Beesley[2] state that "experiments carried out at 19.7 and 25° showed the relative temperature coefficients of the quantum efficiency to increase slowly, but unmistakably, with λ between 313 and 436mμ."

In view of the fact that Franck[15] has shown that chlorine dissociates into an excited and a normal atom as a primary act on absorption of a quantum of frequency greater than the convergence frequency of chlorine (which corresponds to λ4785 Å.), it is difficult to explain the results of Allmand and Beesley.[2] However, if a quantum of light, of wave length greater than 4785 Å. but still containing nearly enough energy to dissociate a chlorine molecule, is absorbed, it is quite probable that the resulting activated molecule can be dissociated by means of a collision.[16] It is very probable that activation of this type does possess a relatively large temperature coefficient.[17] This fact may be responsible for the higher temperature coefficient observed when "green" light (or monochromatic light of 5460 Å.) is used; but it does not explain Allmand and Beesley's result for shorter wave lengths. Since they determined the amount of absorption by measuring the incident intensity and computing the absorption from von Halban and Siedentopf's data,[18] it is possible that the explanation of their results lies in the effect of temperature on the absorption coefficient of chlorine for the several frequencies used.[19]

Temperature Coefficient of the Radiochemical Reaction.—The methods used in determining the temperature coefficient of the radiochemical reaction were similar to those used in the study of the photochemical reaction. The apparatus is represented in Fig. 1. The thermostat surrounding the photochemical vessel was kept at room temperature or at 98°.

Reaction velocity measurements were made alternately, when the activation was due to α-rays alone, and when it was due to both α-rays

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[15] Franck, *Trans. Faraday Soc.*, **21**, 536 (1925).

[16] Compare Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., Inc., New York, **1928**, p. 98.

[17] Compare, however, the results of Jost [*Z. physik. Chem.*, **134**, 92 (1928)], who found no difference in the efficiency of light from either side of the bromine convergence in producing the synthesis of hydrobromic acid.

[18] Von Halban and Siedentopf, *ibid.*, **103**, 80 (1923).

[19] The effect of this phenomenon on the observed values of the temperature coefficient of photochemical reactions has been discussed by Kistiakowsky, Ref. 16, pp. 248–251.

and light. The experimental procedure and the method of averaging have been described in connection with the photochemical reaction. In this case, however, the average so obtained is the ratio of the sum of the two reaction velocities to that of the radiochemical reaction. In order to reduce a series of such values to a common basis, it is necessary to correct for the decay of radon.

$$e^{-\lambda t}\left(\frac{v_q + v_\alpha}{v_\alpha} - 1\right) = e^{-\lambda t}\frac{v_q}{v_\alpha} = \frac{(M/q)_{25^\circ}}{(M/N)_+}$$

Since the work of Porter, Bardwell and Lind demonstrates that the ratio $(M/N)/(M/q)$ is not dependent on sensitivity, these values may be used to obtain $(M/N)_{98^\circ}/(M/N)_{25^\circ}$ by the method already described. The values so computed are not an exact measure of the temperature coefficient, since the total ionization is not independent of the temperature. The ionization is proportional to the density of the gas or inversely proportional to the absolute temperature. Therefore

$$\frac{371^\circ}{298^\circ} \times \frac{(M/N)_{98^\circ}}{(M/N)_{25^\circ}\text{ obs.}} = \frac{(M/N)_{98^\circ}}{(M/N)_{25^\circ}\text{ corr.}}$$

The corrected values were used in computing K_{10}.

To determine the number of ion pairs formed per second per millicurie with the α-ray bulb and reaction sphere used, the sphere was sealed into a manometric system, 182.3 millicuries of radon was placed in the bulb, and the reaction system was filled with a stoichiometric mixture of hydrogen and oxygen at atmospheric pressure. The pressure change was followed for five days, and kE_0/λ was determined, by plotting log $P_{H_2 + O_2}$ against $e^{-\lambda t}$, to be equal to 0.723. This corresponds to 3.23×10^{15} ion pairs per second per millicurie, in a stoichiometric mixture at N. T. P. If it is assumed that the total ionization in the sphere is proportional to the specific ionization of the gas,[20] it follows that the number of ion pairs formed per second per millicurie in an equimolar hydrogen–chlorine mixture is $(1.33/0.527)10^{-3} \times 3.23 \times 10^{15} = 8.15 \times 10^{12}$. At 22° and 740-mm. pressure (average values for the room temperature measurements) the corresponding value is 7.35×10^{12}. The method of computing M has already been outlined. The values of $(M/N)_{98^\circ}$ were corrected to 25° by dividing by the corresponding values of $(M/N)_{98^\circ}/(M/N)_{25^\circ}$.

A plot of K_{10} against $(M/N)_{25^\circ}$ is included in Fig. 2, the experiments being represented as circles. As in the case of the photochemical reaction, the temperature coefficient is a function of the sensitivity.

The Relative Efficiency of Photons and Ions.—The experimental data,

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[20] This assumption is not in general justifiable. However, Porter, Bardwell and Lind[1] point out that the work of Bardwell and Doerner [THIS JOURNAL, **45**, 2593 (1923)] shows that for spheres of less than 3 cm. radius the intensity of ionization is very nearly constant along this path. Therefore, although the method of calibration used here is not exact, the results are probably not in error by more than 10%.

TABLE V

TEMPERATURE COEFFICIENT OF THE RADIOCHEMICAL REACTION

No.	Millicuries of radon	$\frac{(M/N)_{98°}}{(M/N)_{25°}}$ Obs.	$\frac{(M/N)_{98°}}{(M/N)_{25°}}$ Corr.	$\frac{(M)}{(N)} \times 10^{-3}$	K_{10}
1	3.98	1.20	1.49	3.5	1.057
2	3.92	1.67	2.08	2.5	1.108
3	2.91	1.73	2.15	9.5	1.117
4	2.90	1.85	2.30	16	1.128
5	2.44	1.81	2.25	8.5	1.118
6	2.03	2.08	2.58	11.5	1.120
7	2.02	2.18	2.72	12.5	1.147
8	1.45	1.65	2.06	12	1.105
9	1.44	1.58	1.97	12.5	1.098
10	1.41	2.08	2.58	20	1.144
11	1.40	1.93	2.40	19	1.131
12	2.86	2.04	2.54	11.5	1.131
13	2.40	1.93	2.40	13.5	1.125
14	2.22	1.69	2.10	8	1.104
15	2.22	1.75	2.18	7.5	1.109
16	1.93	1.98	2.46	15	1.125
17	1.92	2.28	2.84	22	1.145
18	1.92	2.13	2.65	23.5	1.135
19	1.56	2.08	2.59	22.5	1.133
20	1.55	2.11	2.62	22	1.135
21	1.38	2.20	2.74	29.5	1.142
22	1.38	2.37	2.95	26	1.153
23	1.17	2.52	3.13	36	1.162
24	1.16	2.43	3.03	52	1.156
25	0.94	2.59	3.22	19.5	1.173
26	.94	2.46	3.06	20	1.165
27	.75	2.26	2.81	33.5	1.149
28	.75	2.24	2.79	32.5	1.147
29	.74	2.28	2.84	34	1.150
30	.63	2.62	3.21	49.5	1.171
31	.63	2.50	3.11	49.5	1.164
32	.63	2.44	3.04	49	1.160
33	.55	2.65	3.33	37	1.165
34	.55	2.44	3.04	36	1.163
35	.54	2.68	3.34	53	1.169
36	.54	2.64	3.28	51.5	1.167
37	3.58	1.75	2.18	10.5	1.108
38	3.55	1.79	2.22	7	1.110
39	3.53	1.71	2.13	6	1.104
40	3.51	1.98	2.46	5	1.126
41	3.02	1.75	2.18	4.5	1.108
42	2.96	1.64	2.04	5	1.098

summarized in Tables IV and V, demonstrate that the value of the temperature coefficient of the reaction rate is practically the same for the photo- and radiochemical reactions. This, as well as the fact that the temperature coefficient is a function of sensitivity, indicates that the temperature coefficient is determined by the secondary or chain mechanism[21] and that this mechanism is independent of the form of activation. Additional evidence for this latter point has been presented by Porter, Bardwell and Lind,[1] who have demonstrated that the ratio of the yield per ion pair to the yield per absorbed quantum is independent of the sensitivity of the mixture. For measurements at 25° they find the value of this ratio to be 3.72. They assume that K_{10} for the radiochemical reaction is equal to unity and therefore that the ratio is a function of temperature, probably equal to 2.0 at 100°. However, the measurements of the temperature coefficient presented here indicate that the ratio is independent of the temperature, at least for the range 25 to 100°.

In the determination of the radiochemical temperature coefficient, a number of values of $(M/N)_{25°}/(M/q)_{25°}$, in arbitrary units, were determined. By introducing the number of ion pairs produced per second and the number of quanta absorbed per second (Table III) this ratio may be converted into absolute units.

$$\frac{(M/N)_{25°}}{(M/q)_{25°}}\ \text{absolute} = \frac{q}{E_t \times 7.35 \times 10^{12}} \times \frac{(M/N)_{25°}}{(M/q)_{25°}}\ \text{arbitrary}$$

where 7.35×10^{12} is the number of ion pairs per second per millicurie. The average value of $(M/N)/[E_+ \times (M/q)]_{\text{arbitrary}}$ for three series of measurements (involving three separate charges of radon in the same bulb, 27 determinations in all) is 1.36 ± 0.21. The corresponding value of $(M/N)_{25°}/(M/q)_{25°\,\text{absolute}}$ is 0.92. Since this determination involves an indirect measure of the number of quanta absorbed, as well as possible uncertainties in the quantity of radon, the measurement was repeated under more definite conditions.

A new radiochemical vessel was calibrated by means of the hydrogen–oxygen reaction, and was found to give 9.45×10^{12} ion pair per millicurie for an equimolar mixture of hydrogen and chlorine at 740 mm. and 22°. Without removing the charge of radon this vessel was sealed into a circulating system containing the light absorption cell. The radon was allowed to decay to about 7 millicuries. It has already been shown that under the experimental conditions employed 5.40×10^{13} quanta per second of λ4358 were absorbed by the chlorine. Using a reaction mixture of low sensitivity (M/N about 4000), three series of measurements of $(M/N)/(M/q)$ were made. Two days later, when an attempt was made to repeat the measurements using a more sensitive mixture an explosion ensued which wrecked the entire apparatus. The average value of $(M/N)_{25°}/(M/q)_{25°}$ abs. based upon the three experiments is 1.18. This is in good agreement with the value obtained by the indirect comparison, but is about three-fold smaller than that published by Porter, Bardwell and Lind.

Very recently Allmand and Beesley[2a] have published a preliminary

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[21] Compare Cremer, Ref. 3.

notice of work which indicates that quanta of different wave lengths differ materially in their chemical efficiency. They state that the efficiency curve has a maximum at 4050 Å. If the factor for 4050 Å. is taken as unity, the value for 4358 Å. is 0.67. Therefore, if monochromatic light of 4050 Å. instead of 4358 Å. had been used in these experiments, the values for $(M/N)/(M/q)_{\text{abs}}$. would have been 0.92 × 0.67 = 0.62 and 1.18 × 0.67 = 0.79, within the limits of experimental error still equal to unity. A similar correction must be applied to Porter, Bardwell and Lind's value of 3.72. However, there are apparently two errors in the computation of this value which should be corrected for first. The total number of ion pairs per α-particle should be $2.47 \times 3.72 \times 10^4 = 9.19 \times 10^4$ not 8.45×10^4.[22] Correcting this to 25°

$$9.19 \times 10^4 \times 273/298 = 8.41 \times 10^4 \text{ ion pairs per particle.}$$

This corresponds to $1.003 \times 10^{18} \times 8.41 \times 10^4 = 8.44 \times 10^{12}$ ion pairs/sec. per millicurie, for the total ionization in the bulb. Repeating their graphical determination of the mean wave length of the light absorbed by the chlorine results in a value of 4350 Å., not 4100 Å. as published. In this computation we have used Priest's[23] values for the energy distribution from a 500-watt tungsten lamp.

There appears to be considerable uncertainty in the published values for the extinction coefficient for copper sulfate solution. The values used were graphical averages of the data of Martens and Grunbaum[24] for 0.62 *M* solution, of van der Gon[25] for 1.15 *M* solutions, and of Mecke and Ley[26] for 0.50 *M* solutions. The method of taking the average (particularly in the region 3600 to 5000 Å.) has a large effect on the values for the average wave length of the light absorbed by the reaction mixture, and a still greater effect on the average efficiency term (Allmand's factor). It is apparently one of the chief sources of uncertainty in the corrected value for $(M/N)/(M/q)$ based upon the work of Porter, Bardwell and Lind.[1] No correction was made for the absorption of crown glass, partly because it is practically independent of the wave length for the region 4000 to 6000 Å. and partly because the thickness of the glass in the optical path is not given. The absorption of chlorine is taken from the work of von Halban and Siedentopf.[18]

From these data a curve of the energy absorbed (in arbitrary units) against wave length was plotted. The corresponding curve of relative

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[22] Ref. 1, p. 2609.

[23] Priest, *J. Opt. Soc. Am.*, **6**, 27 (1922). The filament (color) temperature of this 500-watt lamp was 2848°, not 2700°K. as used by Porter, Bardwell and Lind. However, if 2700° were used it would result in an even greater value than 4350 Å. for the mean wave length.

[24] Martens and Grunbaum, *Am. Physik*, **12**, 1004 (1903).

[25] Van der Gon, *Arch. ne'erl*, **7**, 140 (1923).

[26] Mecke and Ley, *Z. physik. Chem.*, **111**, 385 (1924).

number of quanta absorbed against wave length was plotted, and a mean value (4350 Å.) which divided the area under the curve into two equal parts was determined. The corrected value for $(M/N)/(M/q)$ is

$$3.72 \times \frac{4350}{4100} \times \frac{7.84 \times 10^{12}}{8.44 \times 10^{12}} = 3.67$$

Using Allmand and Beesley's[2a] table of efficiency factors and the plot of relative number of quanta absorbed, a curve of relative number of "effective quanta" was plotted against wave length. The ratio of the total areas under these two curves is the efficiency factor (in terms of λ4050 Å.). Using this factor (0.71), Porter, Bardwell and Lind's value of $(M/N)/(M/q)$ reduces to $0.71 \times 3.67 = 2.6$.

The average of these three values for $(M/N)/(M/q)$ is 1.3. Although the close agreement between this value and unity is apparently fortuitous, it is fairly certain that the correct value is not greater than 2.0, and is quite probably unity.

The Mechanism of the Reaction.—While the results presented here indicate that the chain mechanism is independent of the form of activation, they do not offer any direct evidence in regard to the nature of that mechanism. However, it is possible to draw certain conclusions about the mechanism of activation. It is now generally accepted that photochemical activation, by light of wave length less than 4785 Å., can be represented as

$$h\nu + Cl_2 = Cl + Cl'$$

A possible corresponding mechanism for the activation by α-rays is

$$Cl_2^+ + (-) = Cl + Cl' \text{ or } Cl_2^+ + Cl_2^- = Cl_2 + Cl + Cl' \text{ or } Cl_2 + (\alpha) = Cl + Cl^+ + (-)$$

These two equations would indicate a value of unity for the ratio $(M/N)/(M/q)$. If the correct value for this ratio were 2.0, a corresponding activation involving negative molecular ions could be assumed

$$Cl_2^+ + Cl_2^- = 2Cl + 2Cl'$$

Of course, both of these processes might occur simultaneously. The experimental evidence seems to indicate that the latter process occurs less frequently than the former.

There is an apparent inconsistency between the results presented here and by Porter, Bardwell and Lind,[1] which show that an ion is very effective in starting a chain, and the results of Allmand and Beesley,[2a] which show that a quantum of *ultraviolet* light is a relatively inefficient source of activation.

Summary

1. The photochemical (white light) and radiochemical synthesis of hydrogen chloride have temperature coefficients which are identical within the limits of experimental error.

2. The temperature coefficient of this reaction varies with the sensitivity of the reacting mixture. The 10° coefficient has a value of about

1.10 for an average chain length of 2×10^3, and rises to a constant value, or flat maximum, of about 1.20 for an average chain length of 8×10^4.

3. It has been shown qualitatively that the temperature coefficient has a value about 10% higher when "green light" (a $NiSO_4$ filter) is used as the source of activation.

4. An absolute value, of approximately *unity*, for the ratio of the yield per ion pair to the yield per absorbed quantum was obtained using monochromatic light of λ4358 Å. The results of Porter, Bardwell and Lind[1] are discussed, and a correction based upon the work of Allmand and Beesley[4] has been applied.

5. A mechanism of activation, consistent with the results presented here, is outlined.

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THE OXIDATION OF IODIDE ION BY PERSULFATE ION. III. THE IODIMETRIC ESTIMATION OF PERSULFATES

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In the second paper of this series the velocity of the reaction between persulfate and iodide ions in alkaline solutions was reported. The iodine produced disappears almost as fast as formed, producing iodate and iodide (through the intermediate formation of hypoiodite); the liberation of iodine on acidifying was assumed to be quantitative. Some of our experiments suggested that the amount of iodine recovered was slightly low. Consequently the iodimetric estimation of persulfate in neutral and alkaline solutions was carefully compared.

A number of previous investigations have proved that persulfate liberates iodine from potassium iodide with quantitative precision in neutral solution[1] and we have fully confirmed this. The reaction is slow, but can be hastened enormously by inert salts, special catalysts, etc., as shown in the papers mentioned.

Experimental

(1) Liberation of Iodine in Neutral Solution.—We first compared the amount of iodine liberated by potassium permanganate in acid solution with that liberated by an equivalent amount of potassium persulfate in neutral solution. The permanganate was carefully standardized, and the concentrations and conditions used in liberating iodine were well

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[1] See Müller and Ferber, *Z. anal. Chem.*, **52**, 195 (1913); Müller, *ibid.*, **52**, 299 (1913); Schwicker, *ibid.*, **74**, 433 (1928); Zombory, *ibid.*, **73**, 217 (1928). References to other literature will be found in these papers.